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Published in:
Computational and Theoretical Chemistry

DOI:
10.1016/j.comptc.2017.02.001

Publication date:
2017

Computational and Theoretical Chemistry 1116 (2017) 92–95

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Bonding in B_2 and B_2^+: Insights from full configuration interaction and valence bond studies

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ARTICLE INFO

Article history:
Received 14 December 2016
Received in revised form 1 February 2017
Accepted 2 February 2017
Available online 6 February 2017

Keywords:
B_2
B_2^+
Valence bond theory
Full CI
Ab initio calculations

ABSTRACT

Full Configuration Interaction (Full-CI) and Valence Bond Self-Consistent Field (VBSCF) methods have been used to study the electronic structure and bonding in B_2 and B_2^+ molecules. The bonding analysis based on these calculations shows that the B_2 molecule is stabilised due to the formation of a double σ bond, one strong σ-bond together with one second weaker σ-bond, and two weak π bonds. Upon ionization one π electron is removed from the system and B_2^+ is formed, which has a one electron σ bond, instead of a π bond. It has been shown that a few carefully chosen VB configurations are enough to describe the bonding; with these structures, geometrical parameters as well as dissociation energies of these unusual molecular species are in agreement with full-CI results.

1. Introduction

The description of bonding in small molecules remains a challenge: although for simple diatomic molecules chemical bonding seems clear, the situation in C_2 showed that it can still lead to surprises [1–7]. Several theoretical studies, at various levels of theory, have been devoted to describe the chemical bonding in the C_2 molecule. There is, however, still an on-going debate within the chemical community regarding the bond-order in this molecule. Considering the carbon-carbon bond length and the relaxed force constant, C_2 fits in between the molecules containing double and triple C—C bonds, *i.e.*, ethene and ethyne [4,8]. On the other hand, analyses based on full configuration interaction and valence bond calculations [2] and that based on natural orbital functional theory (NOFT) [9] have shown that C_2 and its isoelectronic species (CN^+, BN and CB^-) all possess a quadruple bond: a normal σ bond, two π bonds and one long, weaker, σ bond.

Another molecule that may show similar behaviour, as C_2, is the B_2 molecule. According to a molecular orbital scheme, the valence electronic configuration would be $2\sigma_g^2 2\sigma_u^2 1\pi_u^2$ and it would have a triplet ground state. The bond order according to this model would be 1, as the σ electrons would not contribute to the bonding. Only the two π electrons in the π_u orbitals would contribute to the bonding. This situation is similar to the C_2 case, except that in B_2 the π_u orbitals are half filled, leading to an even weaker π bond than in the C_2 case.

In this report, we study the nature of the bonding in B_2 using full configuration interaction calculations and valence bond calculations, to see if there are similarities in the σ bonding situation to C_2. We also study the bonding in the ionized B_2^+ and B_2^{2+} species, to elucidate the nature of the chemical bonding with only one or no bonding π electrons.

2. Computational details

In all calculations, the cc-pVDZ basis set was used. The full CI calculations were performed using GAMESS-UK [10]. Both 1s orbitals were kept frozen. Initial orbitals were taken from a preceding full valence MCSCF calculation.

The valence bond (VBSCF [11,12]) calculations were performed with TURTLE [13] as implemented in GAMESS-UK. Strictly atomic VB calculations were performed where the orbitals were kept

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http://dx.doi.org/10.1016/j.comptc.2017.02.001
2210-271X/

strictly atomic, and delocal VB calculations were performed in which the orbitals were allowed to delocalise [14].

3. Results and discussion

3.1. Full configuration interaction calculations on B_2, B_2^+ and B_2^{2+}

According to the full CI calculations, the ground state of B_2 is a triplet with a leading valence electronic configuration $2\sigma_g^2 2\sigma_u^2 1\pi_{u,x}^1 1\pi_{u,y}^1$. At the equilibrium distance of 1.632 Å (Table 1), the weight of this configuration is 76.6%. The next leading configuration with a weight of 9.5% is $2\sigma_g^2 1\pi_{u,x}^1 1\pi_{u,y}^1 3\sigma_g^2$, in which the two electrons from the antibonding $2\sigma_u$ orbital are excited to the bonding $3\sigma_g$ orbital.

Ionization of B_2 leads to a wavefunction with a 84.0% weight for the $2\sigma_g^2 2\sigma_u^2 3\sigma_g^1$ configuration. Note that upon ionization, the lowest configuration has no π electrons anymore, and one electron occupies the bonding $3\sigma_g$ orbital. As expected, the dissociation energy becomes lower, and the bond distance increases with respect to that of neutral B_2 (Table 1). Further ionization to B_2^{2+} does not lead to a bonded species, and spontaneous dissociation occurs.

The full CI calculations are indicative that the bonding situation in B_2 is unusual and shows agreement with the bonding situation in for example C_2. A closer analysis of the bonding using valence bond calculations is presented in the next section.

3.2. Valence bond calculations on B_2 and B_2^+

At first, a valence bond calculation was performed with the bonding situation with two electrons in each boron-2s orbital and one electron in the π_x and one electron in the π_y orbitals (VB-1, Fig. 1). In total, six structures were used. The energy as a function of the B-B distance is plotted in Fig. 2 (VB-1). As can be seen, no minima can be found using these structures, and the π-bonds alone in the bonding π_u orbitals are not capable of keeping the atoms together: the nonbonding electrons repel too much to form a stable molecule.

A minimum in the potential energy curve (VB-2, Fig. 2) is obtained when structures are added that describe two σ bonds between the two boron atoms (VB-2, Fig. 1). Using this (12-configuration) VB wavefunction, the calculated dissociation energy is 44.9 kcal/mol, which is only in fair agreement with the full CI dissociation energy (Table 1 and Fig. 2). Correlation in B_2 is apparently extremely important to describe the bonding situation accurately. The atomic orbitals involved in these σ bonds are the s and p_z orbitals of each boron atom (Fig. 3). One strong bond is formed between VB orbitals (1) and (8) with an overlap of 0.77, and one weaker bond is formed between VB orbitals (2) and (7) with an overlap of only 0.09. The VB orbitals (3), (4), (5), and (6) form two π bonds; the overlap between the p orbitals is 0.40.

To improve the quality of the VB wavefunction in VB-local, fourteen more configurations were included in the calculation (VB-3 in Fig. 2). Ten of these have one doubly occupied valence orbital (either orbital 2s or $2p_z$) on either of the two B atoms and four configurations have two doubly occupied orbitals (2s on one atom and $2p_z$ on the other atom). With this (26-configuration) wavefunction,

Table 1
The full CI dissociation energies (kcal/mol), equilibrium distance (Å), and total energy (Hartree) for B_2, and B_2^+.

Molecule	E_{dis}	R	E_{tot}
B_2	59.57	1.632	−49.274884
B_2^+	42.63	2.195	−48.951664

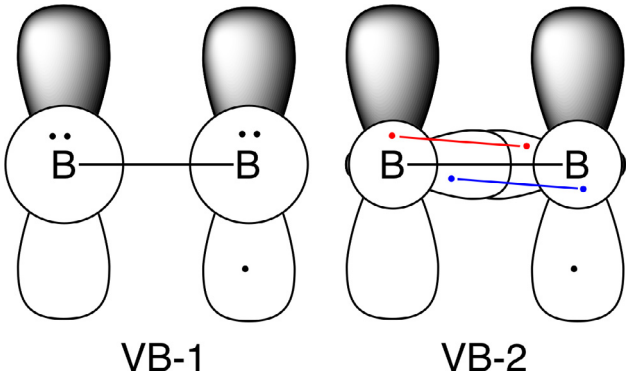

Fig. 1. Different structures considered in the valence bond calculations.

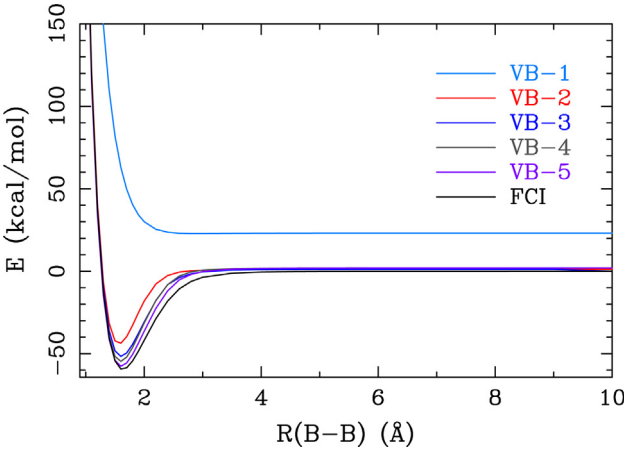

Fig. 2. Dissociation curves for B_2, calculated using different valence bond models and full-CI (see text).

the calculated dissociation energy is 56.65 kcal/mol, which is in very good agreement with the full CI dissociation energy. The equilibrium bond distance is 1.595 Å. At this bond distance, all 26 configurations contribute to the wavefunction. The most important are those, which describe two σ bonds between the two boron atoms. The combined weight of these configurations is 38%. The second in importance are those, which describe two doubly occupied orbitals; their accumulated weight in the wavefunction is 34%. The remaining 28% consists of those configurations, which have one doubly occupied valence orbital on one of the two boron atoms. The general bonding picture of this more accurate wavefunction is similar to the simpler VB-2 description.

Using the delocal model, the dissociation curves have been calculated. The dissociation energy obtained using the 12-configurations wavefunction (VB-4, Fig. 2) is 52.9 kcal/mol, which is substantially better than the dissociation energy obtained using the strictly atomic VB-2 model with the same number of configurations. A similar bonding picture is obtained: the wavefunction consists mainly of only one structure describing one strong σ bond between the valence bond orbitals (5d) and (6d) (Fig. 4), with an overlap of 0.86, and another weaker σ bond between the orbitals (1d) and (2d) (Fig. 4). These orbitals have an overlap of 0.29. Note that the overlap has increased significantly in comparison to the overlap obtained with the strictly atomic model. The two π_u orbitals are both occupied with one electron each.

The dissociation energy calculated using 26-configuration wavefunction (VB-5, Fig. 2) in VB-delocal is 59.60 kcal/mol, which is very close to that obtained with the full CI calculations. The equi-

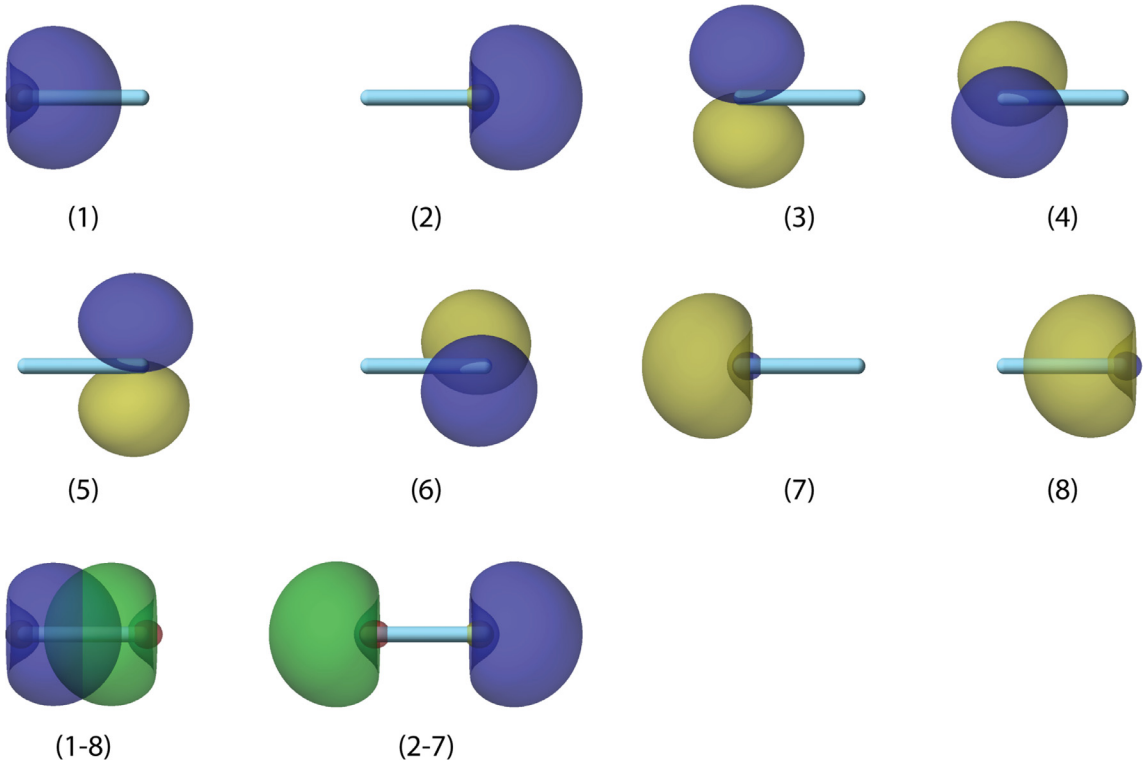

Fig. 3. The strictly atomic valence bond orbitals involved in the bonding.

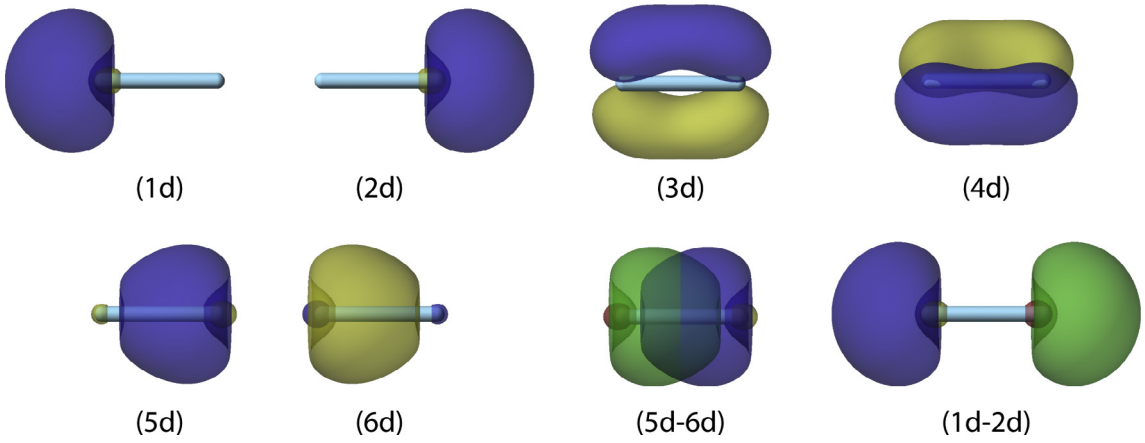

Fig. 4. The delocal valence bond orbitals involved in the bonding of B_2.

librium bond distance calculated using this wavefunction is 1.606 Å, which is also in excellent agreement with that calculated using full CI. This wavefunction gives a very accurate description, in line with the full-CI results, but the main bonding features are already captured by the simpler 12-configuration VB wavefucntion. For comparison, a full valence CASSCF calculation (CASSCF (6,8)) yields a dissociation energy of 59.74 kcal/mol. Smaller active spaces are not well-suited to describe this dissociation. Spin-coupled VB will also give similar results as it is in essence the same as VBSCF, but the latter method is more general.

The valence bond orbitals calculated in the strictly atomic model for B_2^+ are depicted in Fig. 5. In the VB wavefunction, several structures are important: the two main structures with a combined weight of 0.51 describe one doubly occupied 2s orbital (either orbital (1p) or (2p), Fig. 5), a doubly occupied σ bond formed by the orbitals (1p-4p) or (2p-3p), and a singly occupied (3p)/(4p) orbital. The two orbitals involved in the bonding have a small overlap of only 0.01. The next two structures with a combined weight of 0.46 describe two doubly occupied 2s orbitals ((1p) and (2p)) and a singly occupied (3p)/(4p) orbital. The calculated dissociation energy is 40.7 kcal/mol, which is in good agreement with the full CI results (Table 1).

4. Conclusions

This study shows that unusual σ bonding motifs exists in B_2 and B_2^+. In B_2, a double σ bond is formed, of which one is a strong, regular, bond, while the second bond is weaker. Upon ionization, one π electron is removed from the system, while the other π electron prefers to be in a σ orbital. Also in this case, an unconventional σ bond is formed.

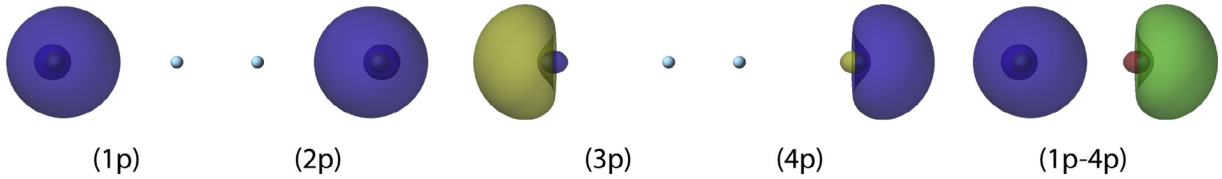

Fig. 5. The strictly atomic valence bond orbitals involved in the bonding of B_2^+.

Acknowledgement

RWAH acknowledges fruitful discussions with Prof. Dr. R. Broer (University of Groningen).

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